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Comments on the application of the Scherrer equation in "Copper aluminum mixed oxide (CuAl MO) catalyst: A green approach for the one-pot synthesis of imines under solvent-free conditions", by Suib et al. [Appl. Catal. B: Environ, 188 (2016) 227–234, doi:10.1016/j.apcatb.2016.02.007]

Suib et al. have recently reported [1] the preparation of a copper aluminum mixed oxide catalyst for the synthesis of imines under solvent-free conditions. Despite the evident interest of the paper, some conceptual mistakes in the characterisation of the samples, especially those concerning determination of crystallite size, should be considered. This Letter is thus concerned not with the interpretation or value of the catalytic results, but with the analysis of some experimental raw data and the information derived thereof.

The samples were prepared by coprecipitation in the presence of different amounts of active carbon, which acted as a sort of template, and which was removed upon calcination at 500 °C in air for 3 h. Upon this treatment, all diffraction maxima recorded were assigned by the authors to the tenorite phase of CuO (ICDD card 80–1916). However, according to data in the literature and in the named card, ascription of the maxima was wrong. The positions (2θ values, when using radiation Cu $K_{\alpha 1}$) of the most intense maxima for this phase, as they appear in card ICDD card 80–1916, are those summarized in Table 1.

In the XRD diagram reported by Suib et al. [1] the two most intense maxima are recorded close to 34.5 and 38° (2θ) and are ascribed to planes (002) and (200), respectively (Fig. 1 [2]). Obviously, due to the closeness (according to Table 1) between the maxima due to planes (11-1) and (002) at 35.496 and 35.410° (2θ), discrimination between them is practically impossible, but the most intense maximum is that corresponding to planes (11-1), and not to (002). A similar situation can be found for the maxima close to $2\theta = 38$–$39°$: the most intense one (100% relative intensity) is that one due to planes (111) at $2\theta = 38.687°$, and not to planes (200), at $2\theta = 38.888°$, as these authors have assumed.

Or, in other words: ascription of the diffraction maxima is wrong or, at least, incomplete.

From the powder diffraction diagram, the minimum value of the crystallite size can be calculated by using the Scherrer equation. More detailed aspects of its use can be found elsewhere [3,4].
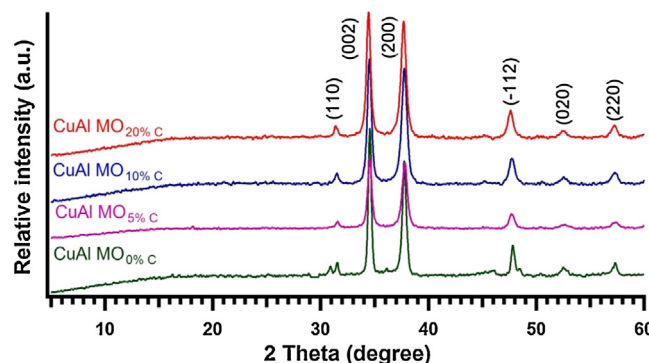

Fig. 1. X-ray diffraction pattern of CuAl MOs synthesized with different amounts of activated carbon [2].

The equation has the general form:

$$L_{hkl} = \frac{K\lambda}{\beta_{hkl}(\theta)\cos\theta} \qquad (1)$$

where:

L_{hkl} is the average crystallite size for an *hkl* reflection.

K is the shape factor, dimensionless, usually taken as 0.89.

λ is the wavelength used, in this case Cu $K_{\alpha 1}$ of Cu and equal to 0.15406 nm.

$\beta_{hkl}(\theta)$ is the full width at half maximum (FWHM) for the *hkl* reflection at 2θ.

The units for L_{hkl} coincide with those for λ. For the evaluation being homogeneous, β_{hkl} should be given in radians, not degrees.

Thus, the crystallize size depends on the *hkl* reflection considered for the calculation at the corresponding angle diffraction. This might be less relevant in the case of isotropic crystals (e. g., cubic ones), but is of paramount importance in the case of anisotropic solids. In the current case, quite surprisingly, despite the authors determine the crystallite size from the XRD data, they do not mention which reflection has been used to perform such a calculation with monoclinic crystals (tenorite) and simply state that when no active carbon was used as a template, the average crystallite size was 27.7 nm, while when 20% of active carbon was used, the average crystallite size was 1.1 nm. We will try to demonstrate that the experimental raw data shown in their paper do not lead to these results.

By using Eq. (1) above, however, we may try to determine which maximum was used to determine the average crystallite size, by using the equation in the form (for simplicity, we do not further indicate *hkl* as a subscript):

$$\beta(\theta)\cos(\theta) = \frac{K\lambda}{L}$$

If the average crystallite size is 1.1 nm, then the product $\beta(\theta)\cos(\theta)$ equals 0.1246 rad, equivalent to 7.139°.

Table 1
Selected diffraction lines for CuO (tenorite) from ICDD card 80-1916.

2θ (deg)	Intensity (%)	*hkl*
38.687	100.0	111
35.496	85.2	11-1
35.410	45.0	002
38.888	22.4	200

As $\cos(\theta)$ has a maximum limiting value of 1.0 for $\theta = 0$, 7.139° is the minimum value of $\beta(\theta)$. That is, the peak used to determine the average crystallite size should have a FWHM larger than 7.139°. This is absolutely in disagreement with the experimental data (XRD patterns) reported by Suib et al. [1], where the value for FWHM is never larger than 1–1.5°.

As mentioned above, the authors did not state which maximum was used to determine the average crystallite size. If we assume that the most intense peak close to $2\theta = 38.6°$ was used, then $\cos(19.3) = 0.9438$. As the FWHM of this maximum is around 1°, then, using Eq. (1) the average crystallite size results 8.3 nm.

We can also assume that for determining the average crystallite sizes for all four samples studied by Suib et al. [1] the same maximum was used. In such a case, $\cos(\theta)$ is a constant for all four samples and thus we can write:

For sample 1: $L_1 \beta_1 \cos(\theta) = K \lambda$
For sample 2: $L_2 \beta_2 \cos(\theta) = K \lambda$

and from the ratio between these equations we can write:

$$\frac{\beta_1}{\beta_2} = \frac{L_2}{L_1}$$

Or, in other words: if the average particle size for the largest crystallites is 27.7 nm and that for the smallest crystallites is 1.1 nm, that means that the ratio between the FWHM values for both samples should be equal to $27.7/1.1 = 25$, and in no case such an extremely large difference between the FWHM values for the sample prepared without or with 20% activated carbon can be seen in Fig. 1.

It is obvious that the average crystallite size should be determined from the best defined maximum in the XRD diagram, but in the current case both intense maxima are actually the result of overlap of two maxima in both cases. As a result, the FWHM measured will be larger than that corresponding to a single maximum, and, as the FWHM is included in the denominator of Eq. (1), the average crystallite size calculated will be always smaller than the actual one.

From the figure reported in [1], it is obvious that the FWHM for the most intense maximum in all for samples (even taking into account that it results from the overlapping of two maxima) is always in the 1–2° range, and thus the differences in the average crystallite size will be never as large as these authors have reported. Probably, by application of refinement analysis (e.g., Rietveld) good fitting of the patterns could be achieved and the FWHM values be determined with more precision.

From this discussion, any conclusion reached and based on the crystallite size of the catalyst used is wrong, as the actual sizes are far from those reported in this paper.

References

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[2] Reprinted from Applied Catalysis B: Environmental, Vol. 188 Madhavi N. Pahalagedara, Lakshitha R. Pahalagedara, David Kriz, Sheng-Yu Chen, Forrest Beaulieu, Wimalika Thalgaspitiya, Steven L. Suib, Copper aluminum mixed oxide (CuAl MO) catalyst: a green approach for the one-pot synthesis of imines under solvent-free conditions, Appl. Catal. B: Environ. (2016) 227–234, Copyright (2016), with permission from Elsevier.

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